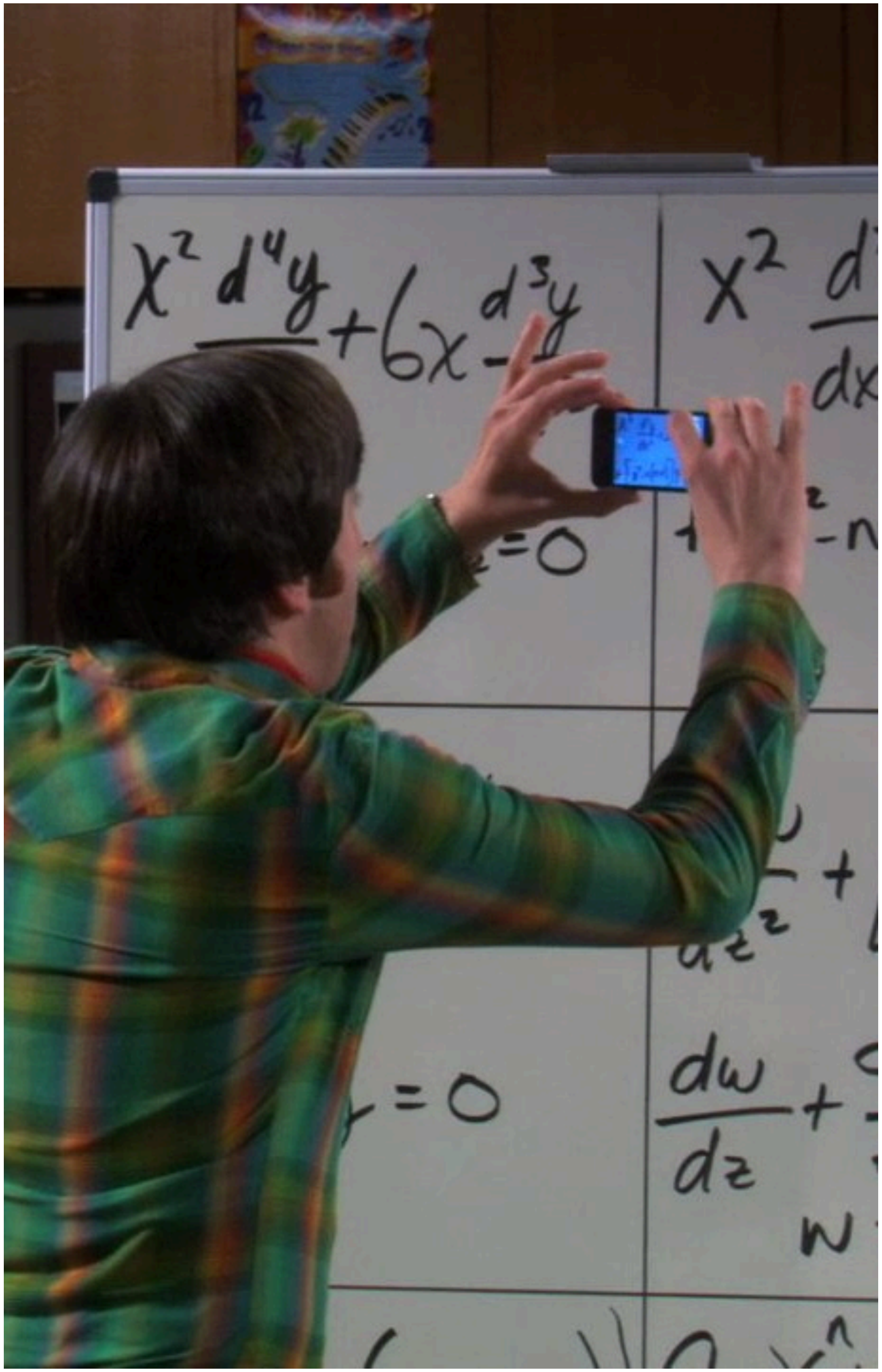
- **<u>Theme Music:</u> Desi Arnaz**

  Perhaps, perhaps, perhaps

- **<u>Cartoon:</u> Pat Brady**

  Rose is Rose



The Equation of the Day

Gibbs Free Energy

$$\Delta G = \Delta H - T\Delta S$$

How is entropy extensive?

- W_{A} = number of microstates for system A
- W_{B} = number of microstates for system B
- $W_{\mathrm{total}} = W_{\mathrm{A}} W_{\mathrm{B}}$
- $S_{\mathrm{A}} = k_B \ln W_{\mathrm{A}}$
- $S_{\mathrm{B}} = k_B \ln W_{\mathrm{B}}$
- $S_{\mathrm{total}} = k_B \ln (W_{\mathrm{A}} W_{\mathrm{B}}) = k_B \ln W_{\mathrm{A}} + k_B \ln W_{\mathrm{B}}$
- $S_{\mathrm{total}} = S_{\mathrm{A}} + S_{\mathrm{B}}$

Doubling the size of the box

- $W_1 = M^N$
- $W_2 = (2M)^N = 2^N M^N = 2^N W_1$
- What does this say about the change in entropy when the size of the box is doubled?
- $S_1 = k_B \ln W_1$
- $S_2 = k_B \ln W_2 = k_B (N \ln 2 + \ln W_1) = k_B N \ln 2 + S_1$

Foothold ideas: The Second Law of Thermodynamics

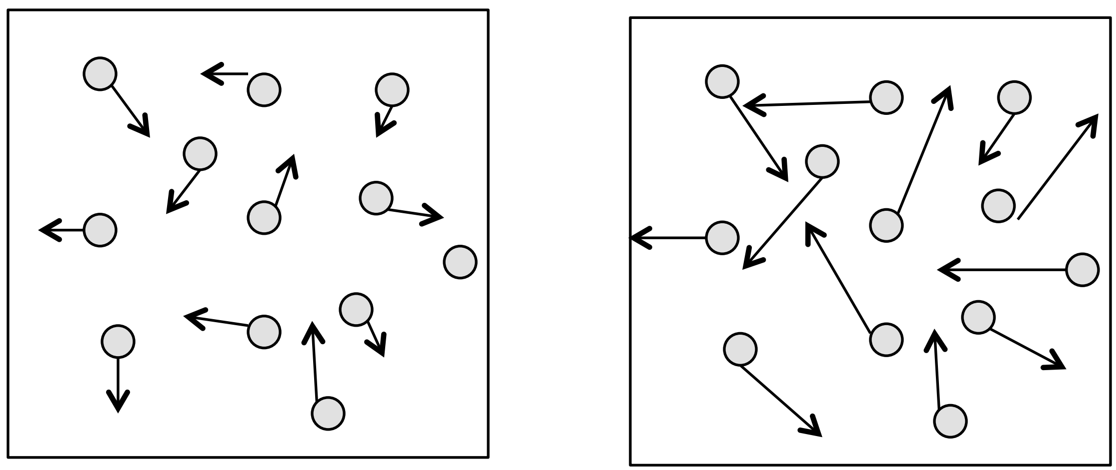
- Systems spontaneously move toward the thermodynamic (macro)state that correspond to the largest possible number of particle arrangements (microstates).
  - The 2^{nd} law is probabilistic. Systems show fluctuations – violations that get proportionately smaller as N gets large.
- Systems that are not in thermodynamic equilibrium will spontaneously transform so as to increase the entropy.
  - The entropy of any particular system can decrease as long as the entropy of the rest of the universe increases more.
- The universe tends towards states of increasing chaos and uniformity. (Is this contradictory?)

Conclusion

- If energy packets are randomly fluctuating through all DoFs with equal probability, then each microstate will be equally probable.
- Some macrostates (distributions of energy between blocks of the system) are more likely.
- Thermal energy is more likely to flow from a hot object to a cold object than vice versa – and the more DoFs there are, the stronger this tendency will be.

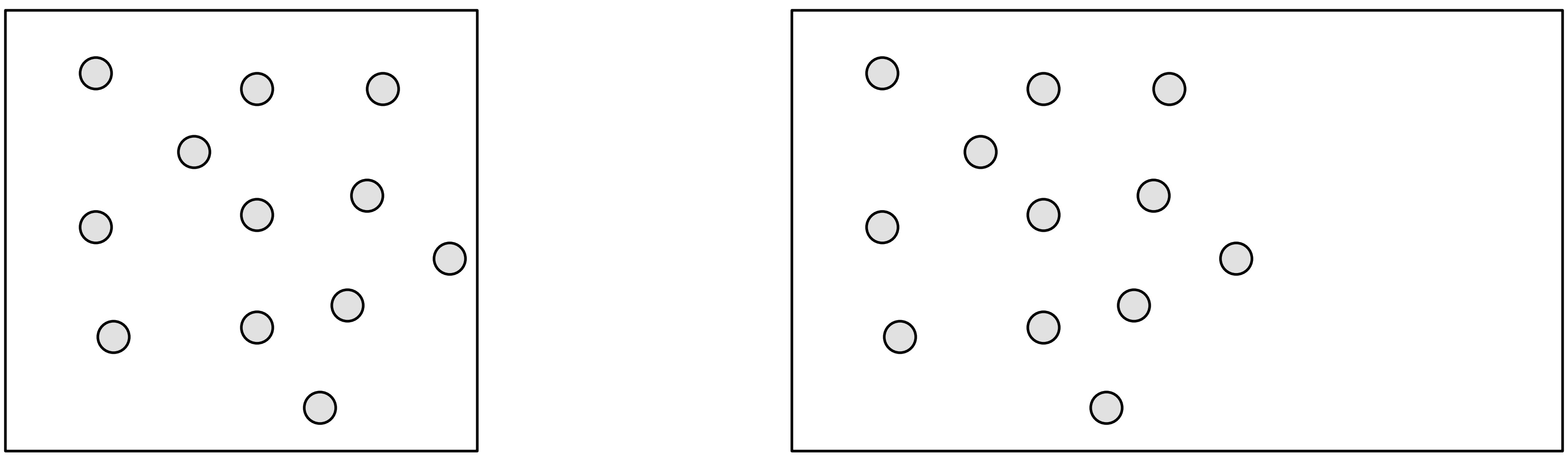
Ways to increase entropy

- Add energy



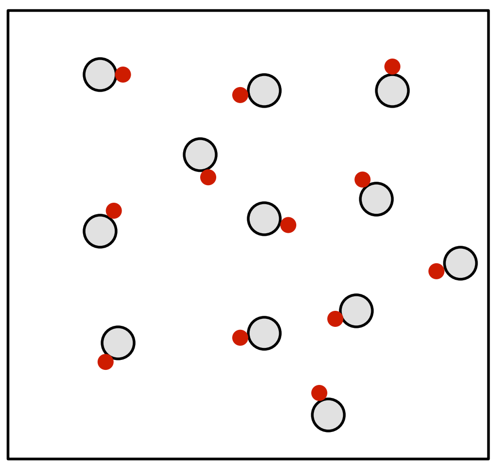
Ways to increase entropy

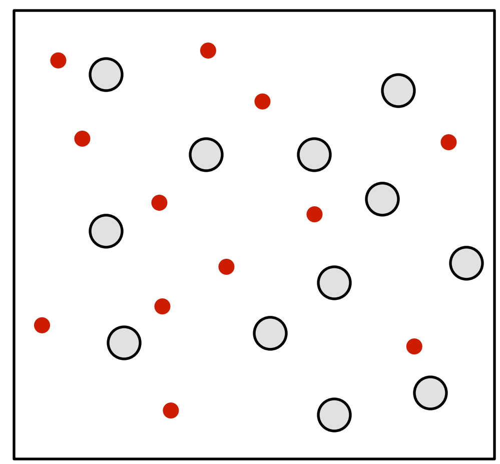
- Increase volume



Ways to increase entropy

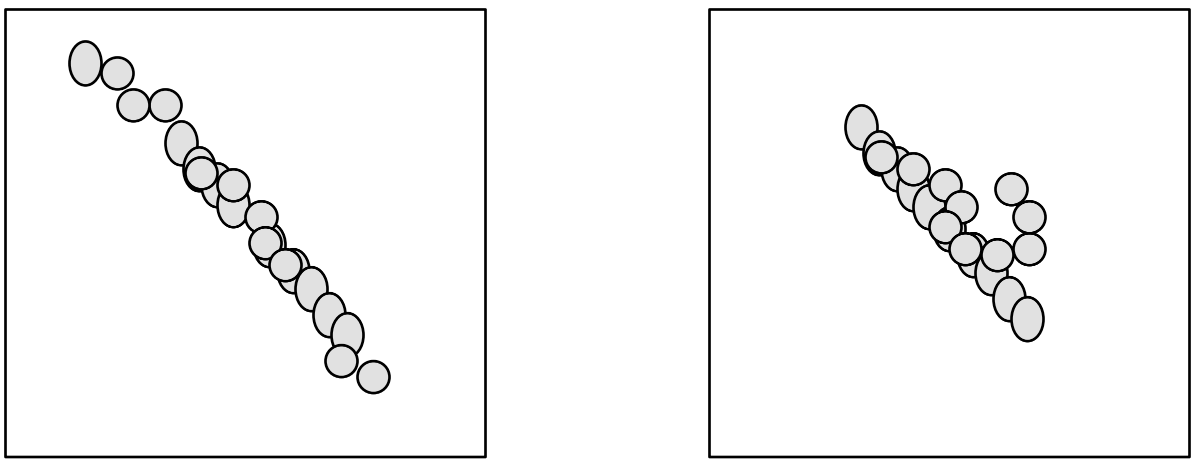
- Decompose molecules





Ways to increase entropy

- Let a linear molecule curl up



What?! Why!

Conditions on a spontaneous change due to energy exchange

- Consider some system spontaneously transforming by exchanging some energy, $\Delta U_{sys} = Q$, with its environment.
  Two conditions must be met:
- First law: $\Delta U_{sys} + \Delta U_{env} = 0$
- Second law: $\Delta S_{sys} + \Delta S_{env} \geq 0$

- Entropy-energy relation: $\Delta S_{env} = \dfrac{\Delta U_{env}}{T} = -\dfrac{\Delta U_{sys}}{T}$

These let us express the condition on the change of entropy of the universe in term of the system alone.

$$\Delta S_{env} = -\frac{\Delta U_{sys}}{T}$$

$$\Delta S_{sys} + \Delta S_{env} = \Delta S_{sys} - \frac{\Delta U_{sys}}{T} \geq 0$$

$$T\Delta S_{sys} - \Delta U_{sys} \geq 0$$

$$\Delta U_{sys} - T\Delta S_{sys} \equiv \Delta F \leq 0$$

If we are operating at constant pressure, we want to use enthalpy, ΔH, instead of internal energy, ΔU. This yields Gibbs FE (G) instead of Helmholtz FE (F).

Foothold ideas: Transforming energy

- Internal energy: thermal plus chemical ΔU
- Enthalpy: internal plus amount needed to make space at constant p $\Delta H = \Delta U + p\Delta V$
- Gibbs free energy: $\Delta G = \Delta H - T\Delta S$ enthalpy minus amount associated with raising entropy of the rest of the universe due to energy dumped
- A process will go spontaneously if $\Delta G < 0$.

Reading question

- Is Gibbs free energy conserved like all other energy?